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THE PHOTOCHEMICAL BEHAVIOR OF OXYGEN-CONTAINING COMPLEXES
IN ALKALI HALIDE CRYSTALS

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ABSTRACT

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The optical absorption spectra of KCl, KBr and KI crystals with small contents of hydroxyl ions and other oxygen complexes are measured before and after irradiation with unfiltered light from an hydrogen discharge lamp. The measurements are extended over λ 180 to 800 m μ . At low temperatures hydroxyl ions are photochemically dissociated into oxygen ions and hydrogen atoms at interstitial positions. The hydrogen atoms are identified by paramagnetic spin resonance experiments similar to those of Delbecq, Smaller and Yuster on KCl-KH crystals. The optical properties and the thermal stability of the interstitial hydrogen are discussed and compared with older measurements on KH-doped crystals.

Author

1. Introduction

Alkali halide crystals with oxygen-containing additions were first investigated by Hilsch and Pohl (Ref. 1). Subsequent to their investigations, von Lupke (Ref. 2) found that, in crystals to which KOH, K₂O₂ and K₂CO₃ had been added, color centers are produced upon irradiation of the oxygen complex bands with light at room temperature. More recently, Rolfe (Ref. 3) has irradiated KOH-containing crystals at lower temperatures and has shown that the photochemical behavior of hydroxyl-containing crystals is similar to that of crystals containing hydrides. Hilsch and Pohl (Ref. 4) have found that hydride-containing crystals represent excellent model substances for the investigation of photochemical reactions.

The present work investigates in detail the course of the photochemical reactions in crystals that contain oxygen-containing complexes. Measurements of the optical absorption and paramagnetic resonance are carried out for this purpose. The interpretation closely follows the explanations of Delbecq, Smaller and Yuster (Ref. 5) concerning the occurrences in hydride-containing crystals.

2. Experimental Details

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The investigations were carried out on single crystals of KCl, KBr and KI drawn from the melt in air. The content of the melt of oxygen-

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containing additions amounted to approximately 0.1 mol percent. Water-cooled hydrogen lamps from Kern and Sprenger, Goettingen, were used for the irradiation of the crystals. The optical measurements were performed on a Zeiss monochromator (measuring range 210 to 1,00 $m\mu$) and on an U.V. recording monochromator which was built at this institute (measuring range 180 to 300 $m\mu$). During the measurements and irradiation, the crystals were kept in a cooling pot, similar to the one described by Kaiser (Ref. 6). All optical measurements were performed with a comparison crystal.

A Varian instrument that operates in the 3-cm area was used for the measurements of the paramagnetic resonance. The crystals were held in the cooling pot, Figure 1, both during irradiation and measurement. The dimensions of the crystals were approximately 2 x 2 x 30 mm, and the heat-transfer to the crystal took place through copper clamps and General Electric adhesive 703-1. The cooling pot was connected to the vacuum pump during the irradiation, but it was removed from the vacuum aggregate during electron spin resonance measurements. The upper part of the pot contained activated charcoal at low temperature for the absorption of any remaining gases. The inner portion of the pot could be turned in reference to the outer portion by means of a greased ground-glass surface for the purpose of orienting the crystals in the magnetic field.

The quartz tube of the cooling pot showed no paramagnetic resonance absorption throughout the entire measuring range.

3. Measurement Results on Hydroxyl-Containing Crystals

a) Optical Measurements

Figures 2 and 3 indicate, in partial curves, the absorption of a KCl and a KBr crystal with KOH addition at 78°K. As the temperature is reduced, a slight shift of the maximum toward the shorter wavelength takes place. This is shown by the example of the KCl + KOH in Figure 4. Equal bands are obtained upon addition of K_2CO_3 , K_2O_2 , as well as KCN to

the melt, as was shown by von Lupke (Ref. 2). According to Etzel and Patterson (Ref. 7), all of these additions produce the typical absorption of the OH^- radical in the infrared. This leads to the conclusion that KOH is formed from these additions because of decomposition at the high melting temperature.

In addition to the common OH^- absorption, Korth (Ref. 8) and Maslakowez (Ref. 9) also measured the typical vibration bands of K_2CO_3 and

KCN in the infrared upon addition of these radicals. These results indicate that a certain portion of the additions is built into the crystals without being decomposed.

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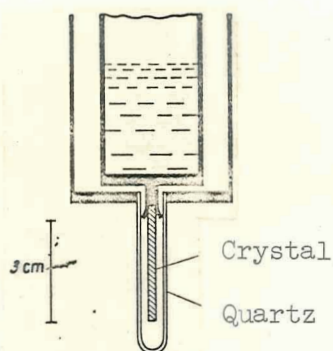


Figure 1. Cross section of the lower portion of the cooling pot for paramagnetic spin resonance measurements. The design permits the irradiation of the deeply cooled crystal with ultraviolet light and its inclusion in a hollow core resonator for the resonance measurement. The resonator has a corresponding bore

The partial curve b in Figures 2 and 3 shows the absorption spectra of the crystals after a 45 minute irradiation at 78°K with a water-cooled hydrogen lamp. The OH⁻ band is partially decomposed by the irradiation, and two new absorption bands are produced. The long wave band was first measured in connection with a KOH addition by Rolfe (Ref. 3) and was identified for KCl with the U₂ band that was measured by Delbecq, Smaller

and Yuster in KCl + KH. The long wave band in KBr is, according to its position, identical to the U'' band (see Figure 7) which was found by Thomas (Ref. 10) in KBr + KH crystals. After irradiation of KCl + KOH, Rolfe has also obtained the F and U₁ bands and the F and V₁ bands in

KBr + KOH. These bands can be located only after a two-hour irradiation (see Figure 5) and they only appear when the U₂ and U'' absorption has

attained a certain value. The band that was produced on the short wavelength side of the OH⁻ maximum is more pronounced in KCl than in KBr and it corresponds, in its half-value width, approximately to the U₂ band.

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It is not identical to the α band, as had been assumed by Rolfe (Ref. 3).

The partial curves c and d of Figures 2 and 3 indicate measurements at 78°K, first after warming of the irradiated crystals to 130°K, secondly after warming to 300°K. The U₂ band is completely decayed in KCl upon heating to 130°K. The wide and unsymmetrical U'' band is reduced in KBr to a small remainder on the short wavelength side. In both cases color centers appear, and the F band in KCl is strongly widened. The short

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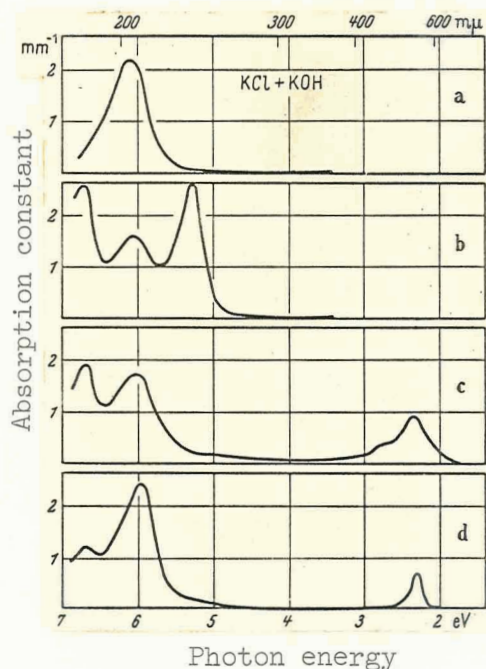


Figure 2a-d. Absorption spectra of KCl crystals with 0.1 mol percent KOH. All measurements at 78°K.

a, initial condition; b, after irradiation with ultraviolet light at 78°K; c, after warming to 130°K; d, after warming to 300°K

wave absorption beyond the OH⁻ band is partially decomposed in KCl and completely decomposed in KBr. In the case of KBr, an indication of the bands α (6.15 eV) and β (6.44 eV) is present. These bands are beyond the measuring range in the case of KCl. During the warming to 130°K, a definite luminescence is observed in the case of KBr, and the emission is primarily in the ultraviolet. (Demonstrated with a photocell and uranyl glass.) When 130°K has been reached, the thermoluminescence is finished. Such a luminescence could not be demonstrated in KCl.

After additional warming to 300°K (sections d, Figures 2 and 3), a longer wavelength absorption was originated in the KBr and KCl instead of the original OH⁻ bands. This has been assigned by Rolfe to an O²⁻ absorption. When warmed to 300°K, the broadening of the F bands disappears in KCl, and the shortwave maximum is reduced more and more. In KBr the α and U'' bands wash out completely. On the other hand, the F bands and the β bands that always accompany them are appreciably enhanced.

The same photochemical behavior is also found in crystals with other oxygen-containing additions such as K₂CO₃, K₂O₂, and KOCN. This is shown

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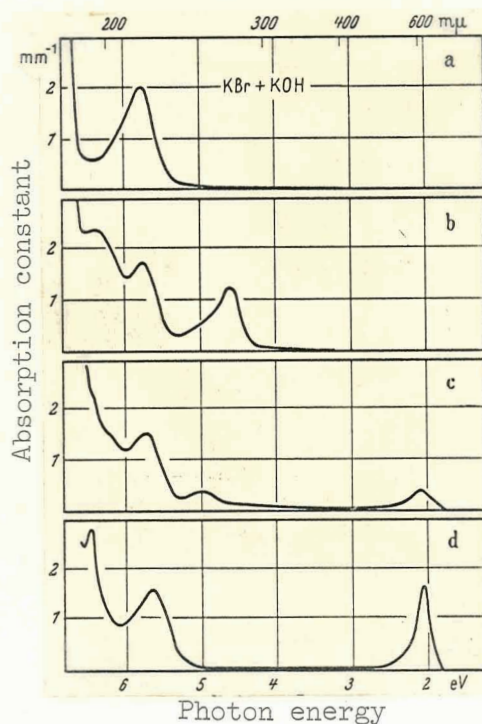


Figure 3a-d. Absorption spectra of KBr crystals with 0.1 mol percent KOH. All measurements at 78°K.

a, initial condition; b, after irradiation with ultraviolet light at 78°K; c, after warming to 130°K; d, after warming to 300°K

in Figure 5 for the examples of $\text{KCl} + \text{K}_2\text{CO}_3$ and $\text{KBr} + \text{K}_2\text{CO}_3$. Three

measurements are given for each crystal: in the upper part, the original condition, in the middle, after irradiation at 78°K and in the lower part after warming to 300°K. The curve shows good agreement with the measurements in KOH-containing crystals. Because of the longer irradiation time (approximately three times as long as in Figures 2 and 3), the V_1 band

appears at 3.02 eV in $\text{KBr} + \text{K}_2\text{CO}_3$. At the same time, the OH^- band is

superimposed by a longer wavelength absorption, so that the absorption peak now appears to be shifted toward the longer wavelengths.

A similar shift is obtained by the attachment of electrons at higher temperatures¹. This was also observed by Etzel and Patterson (Ref. 7).

¹Immigration of electrons in the electrical field at 580°C, subsequent removal of the unattached electrons through field reversal.

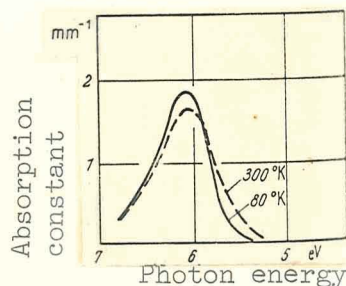


Figure 4. Temperature dependence of the OH^- absorption band in KCl

The photochemical behavior of the crystals is, however, not changed by this measure.

In the case of KI with KOH addition, the considerably longer wavelength self-absorption that sets in interferes with these investigations. The OH^- band is, even at low temperatures, considerably obscured by its self-absorption. On the long wavelength side upon irradiation at 78°K , we do not obtain any of the U_2 or U'' bands in a well defined form.

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b) Electron Spin Resonance Measurements

Figure 6 presents the measurements of the paramagnetic resonance in KCl + KH and KCl - KOH crystals at a measuring temperature of 80°K , and represents a direct reproduction of the strip chart. The derivation of the absorption is presented after the magnetic flux density versus the magnetic flux density. Curve d indicates the microwave signals which were measured after a one-hour irradiation of a KCl + KH crystal at 80°K . The irradiation takes place by the unfiltered light of two hydrogen lamps in opposing position. Only a few color centers are formed within the volume of the crystal during the irradiation. This measurement was carried out to ascertain the measuring arrangement according to the data obtained by Delbecq, Smaller and Yuster (Ref. 5) on KCl + KH. In agreement with these authors, two absorption bands were found with a distance of 500 (± 10) gauss; the line width is approximately 55 gauss. According to Delbecq, Smaller and Yuster (Ref. 5), this double signal is produced by the spin resonance absorption of hydrogen atoms in interstitial spaces.

The curves 6a, b and c present measurements on KCl + KOH. No signal is obtained in the unirradiated form. Curve a shows the microwave signals obtained after irradiation for 45 minutes at 80°K . Both signals have the same distance as in curve d, the line width is approximately 60 gauss. The difference as compared to curve d is within the limit of accuracy for the measurement. Curve b shows the disappearance of the doublet after warming to 130°K . The signal that now appears may be ascribed to the

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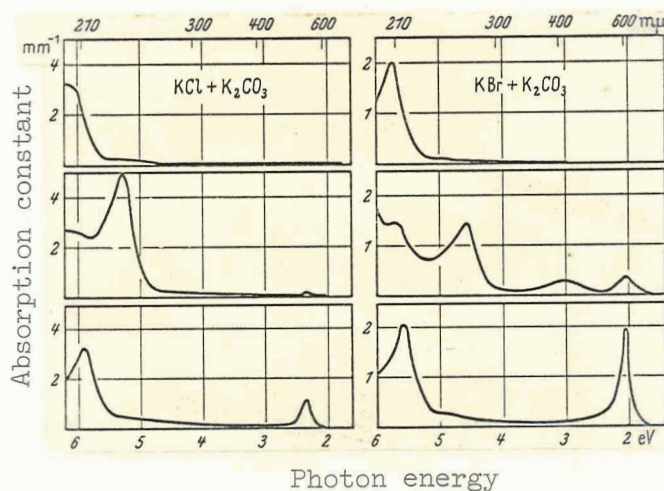


Figure 5. Optical absorption of KCl and KBr crystals with K_2CO_3 addition (content approximately 10^{-3}). All measurements at $78^\circ K$. Upper curves: original condition. Middle curves: after UV irradiation at $78^\circ K$. Lower curves: after warming to $300^\circ K$

color centers that originated through warming. The position and signal width agree with the values that were measured on color centers by Kip, Kittel, Levy and Portis (Ref. 11), and by Delbecq, Smaller and Yuster (Ref. 5). The color center signal disappears upon further warming to $300^\circ K$ (curve c), probably because of colloid formation. However, the discoloration of the crystal is still optically visible.

Corresponding measurements were carried out on KBr + KOH crystals, but these did not produce any signals that could be assigned with certainty to atomic hydrogen. We must, however, expect a considerably lower accuracy of measurement since the half value width of the color center resonance in KBr, which is three times as wide, forces one to expect a considerably greater width of the hydrogen resonance line.

When the measuring range was extended to lower temperatures ($20^\circ K$), these resulted in a superimposition of a fine structure on the resonance absorption presented in Figure 6a and d. This fine structure is dependent upon the orientation of the crystal in the magnetic field, and this orientation dependence is not present in the double band shown in Figure 6a and d. The fine structure appears in both, KCl + KOH and KBr + KOH, and the distance between the fine structure components is considerably larger in the KBr than in the KCl. The fine structure is currently being further investigated and is to be discussed in a future publication.

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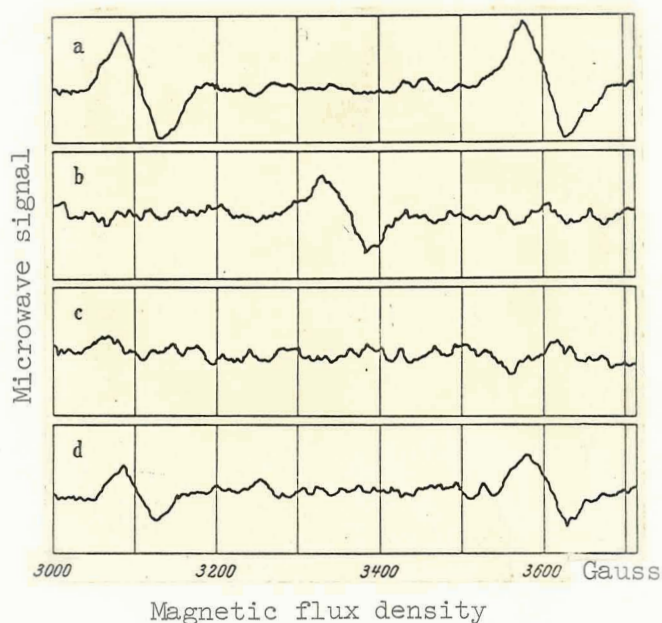


Figure 6a-d. Spin resonance measurements on KCl crystals at 80°K.

a, KCl + KOH after UV irradiation at 78°K; b, KCl + KOH after warming to 130°K; c, KCl + KOH after warming to 300°K; d, KCl + KH after UV irradiation at 78°K

4. Explanation of the Results of the Measurements

KCl and KBr crystals with KOH additions indicate considerable similarity in their photochemical behavior to KCl and KBr crystals containing KH. Hydride-containing alkali halide crystals were thoroughly investigated by Hilsch and Pohl (Ref. 4), Thomas (Ref. 10), Martienssen (Ref. 12) and Delbecq, Smaller and Yuster (Ref. 5). Some results that are important to the interpretation of the photochemical behavior of KOH-containing crystals are to be mentioned initially.

KCl or KBr crystals with KH additions have a well defined absorption band in the UV with peaks at 212, or 224 m μ ($T = 78^\circ\text{K}$), respectively. This absorption is designated as the U band and is originated by H^- ions in anion locations.

Irradiation into the U bands in KCl produces at low temperatures, according to Delbecq, Smaller and Yuster (Ref. 5), a wide band designated as U_1 which extends from 240 to 300 m μ as well as a shorter wavelength band, designated as U_2 with a peak at 236 m μ . Irradiation into the U_1

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bands at 78°K produces color centers and the enhancement of the U_2 band.

After the U_2 band was formed, the authors obtained that paramagnetic resonance absorption which is assigned to the absorption of neutral hydrogen atoms in interstitial location. A corresponding measurement is presented in curve d of Figure 6.

Optical measurements by Thomas (Ref. 10) and Martienssen (Ref. 12) are available on KBr + KH and agree with the measurements on KCl + KH. After irradiation into the U bands at low temperature a wide absorption takes place (see Figure 7), which has been assigned "U" by Thomas. Analogous to KCl, this band should be considered U_1 , according to Delbecq,

Smaller and Yuster (Ref. 5). A clearly defined U_2 band is not obtained.

During irradiation of light from the region of the U" bands, Thomas finds an enhancement of the peak at 270 mμ; color centers are produced in this process and the α band (Thomas terms it U') is suppressed. The same reaction, therefore, takes place as after the irradiation into the U_1 bands

in KCl: the partial conversion of the U_1 band into U_2 . The difference in comparison to KCl is found only in the fact that these two bands overlap considerably in KBr and that, therefore, the transition $U_1 \rightarrow U_2$ is hard to recognize. In Thomas' work, the U_1 and U_2 bands are not differentiated and are, in common, called U".

The photochemical behavior of hydride-containing KCl and KBr crystals at low temperatures can, in summation, be described as follows¹:

(1)

The hydrogen ions H_i^- in interstitial spaces cause the U_1 band, and spaces in the anion lattice cause the α band. Absorption in the U_1 band separate the electron from the hydrogen ion H_i^- :

¹According to Delbecq, Smaller and Yuster (Ref. 5), the meanings are as follows: e = electron; □ = space in the anion lattice (α-center); ⊗ = electron in a space (color center); $[H^-]$ = hydrogen ion in space (U-center); H_i^- = hydrogen ion in an interstitial space (U_1 -center); H_i^0 = hydrogen atom in an interstitial space (U_2 -center).

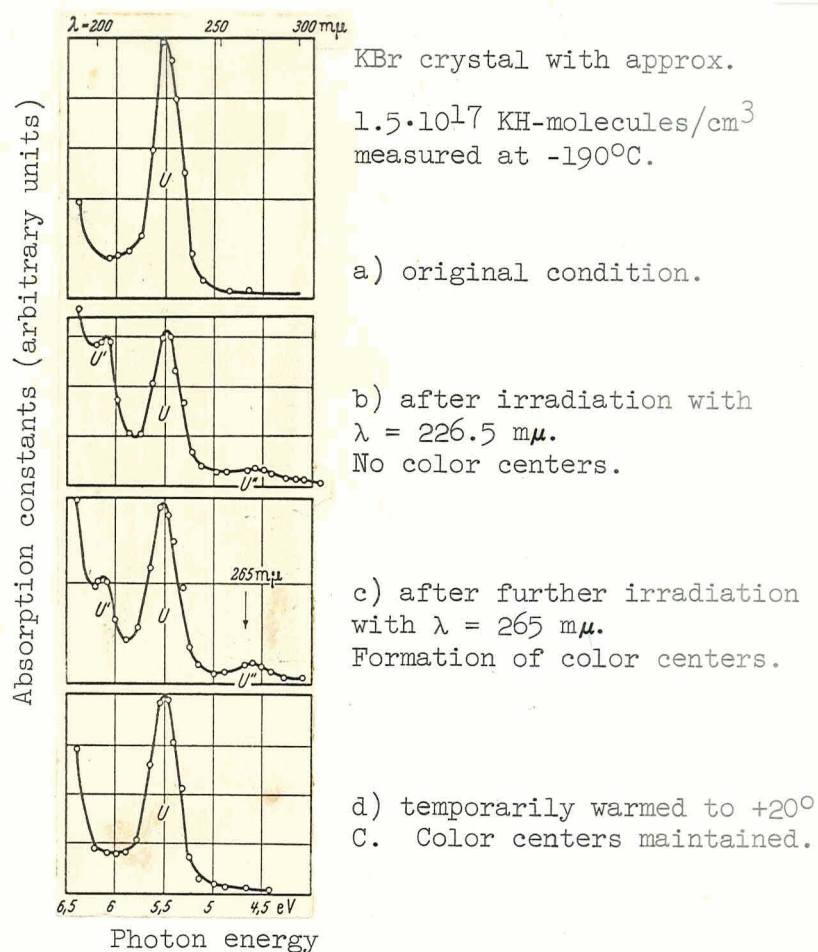


Figure 7. Absorption spectra of KBr crystals with KH addition (from Thomas)



Neutral hydrogen H_i^0 in an interstitial space may be recognized by the U_2 band.

The free electron, originated in (2), is capable of reacting either with spaces under formation of color centers or under the cooperation with spaces and hydrogen atoms to U-centers:



The reactions (3) and (4) become particularly apparent when the crystals are warmed.

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KCl and KBr with KOH addition. To explain the photochemical occurrences in KOH-containing crystals we begin with the assumption that the OH^- ions in the crystal replace individual halogen ions, analogous to the H^- ions in hydride-containing crystals.

After irradiation into the OH^- bands at low temperatures, band U_2 is produced which indicates that neutral hydrogen ions are in the interstitial space, and have been split off by the light from the OH^- complexes. This may be described by the following equation¹:

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We assume that the absorption on the short wavelength side of the OH^- bands was caused by the O^- ions in anion spaces which were thus formed.

It should be noted that, in contrast to hydride-containing crystals, a much higher U_2 band is formed. In experiments on KOH-containing crystals, the area under the U_2 band corresponds roughly to the reduction of the area below the OH^- bands. The oscillator strengths of the OH^- bands and the U_2 bands are, therefore, approximately equal. In KH-containing crystals, the U_1 band is generally obtained after irradiation. The area under the U_1 and U_2 bands is not comparable with the area in the disappearing U bands. We may conclude from this that the oscillator strength of the U_1 centers is considerably smaller than 1.

The U_2 band disappears upon warming to 130°K and the hydrogen atoms in the interstitial spaces form H_2 molecules which can no longer be observed in the absorption spectrum. Additionally, the O^- band is reduced. In this process spaces and electrons are freed:



Part of these spaces and electrons react according to equation (3) and become color centers, or they react with hydrogen atoms and form U centers, and the U band thus formed becomes superimposed on the OH^- band. This may be seen from the slight shift of the absorption peak toward the longer wavelengths.

¹ $[\text{OH}^-]$, $[\text{O}^-]$ hydroxyl, respectively, oxygen ion in a lattice space.

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Upon additional warming to 300°K, the structure of the U bands becomes particularly clear. As may be seen from Figures 2d and 3d, this warming leads, in KCl, primarily to the formation of U centers while, on the other hand, in KBr, color centers are primarily formed. We may conclude from this that the hydrogen formed according to equation (5) can be separated more rapidly as H_2 molecules in KBr than in KCl, so

that the reverse reaction to U centers is not as simple in KBr.

5. Crystals with KNO_3 Additions

KCl and KBr crystals with KNO_3 additions have practically the same absorption in the ultraviolet as do the KOH-containing crystals. As has been shown by Smakula (Ref. 13), in the case of these additions, another band, approximately 100x smaller, is produced at 360 $m\mu$. Hutchinson and Pringsheim (Ref. 14) have recently found a characteristic fine structure in an extensive study concerning the behavior of nitrite-containing alkali halides.

Crystals with nitrate content, after irradiation at room temperature, form, in contrast to KOH-containing crystals, no color centers. On the other hand, upon irradiation of several hours duration by a mercury lamp, the absorption at 360 $m\mu$ (in the case of KI at 450 $m\mu$) is enhanced. (See also Figure 8.)

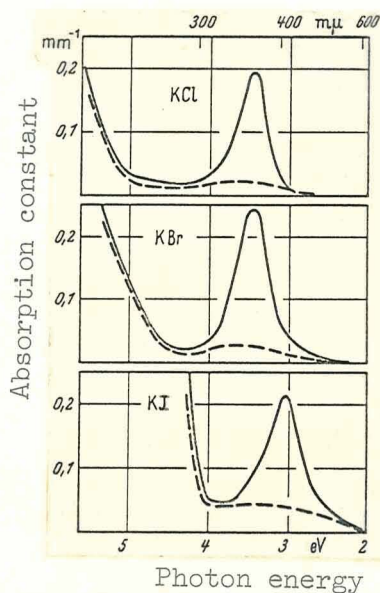


Figure 8. Absorption spectra of KCl, KBr and KI crystals with additions of 1 mol percent of KNO_3 , measured at 300°K.

----- original condition; — after UV irradiation at 300°K

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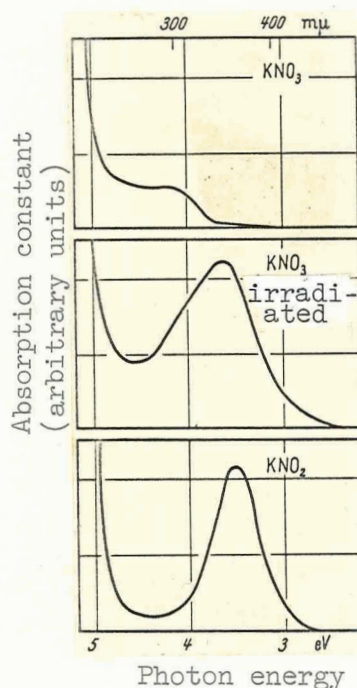


Figure 9. Thin layer absorptions of KNO_3 and KNO_2 at room temperature. The layers are melted upon quartz plates (thickness approximately 0.1 mm). Upper curves: KNO_3 . Middle curves: same layer after several hours of UV irradiation. Lower curves: absorption of a KNO_2 layer

According to Maslakowez (Ref. 8) and Pringsheim (Ref. 15), this absorption is caused by NO_2^- ions in the crystal, and the increase of this absorption also indicates a conversion of KNO_3 to KNO_2 .

A corresponding conversion was also observed by Narayanswamy (Ref. 16) upon the UV irradiation of pure KNO_3 . He has been able to prove the

KNO_2 that was formed by means of chemical methods. Figure 9 shows cor-

responding optical measurements. The upper part presents the absorption of a thin layer of KNO_3 that had been melted on a quartz plate (thickness approximately 0.1 mm). The lower portion shows the absorption spectrum of a similarly produced layer of KNO_2 . The center portion

shows the spectrum of a KNO_3 layer after a three-hour irradiation with a mercury lamp at room temperature. The absorption determined can clearly be derived from KNO_2 formed in the crystal.

I wish to thank Prof. Dr. R. Hilsch and Dr. W. Martienssen for the suggestion and support of this work. I am also very indebted to Prof. R. W. Pohl for his support. Funds were important to this work which had been obtained by Prof. Hilsch from the Deutschen Forschungsgemeinschaft as well as from the Research Corporation. My sincere gratitude is expressed to both these organizations.

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